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Phase II: Laboratory Investigation of Portable Instruments for Submarine Air Monitoring

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14. ABSTRACT

Dräger tubes are currently used to supplement the atmosphere analysis measurements made aboard US Navy submarines. The submarine fleet has requested that these tubes be replaced with a less labor intensive measurement system. Due to recent developments in gas sensing instrumentation, it is possible to replace many of the existing detectors with instruments that will incorporate more than one sensor at a time. This report is a continuation of an evaluation of portable instruments for use in submarines as air monitors. This is the second phase of a three-phase program concerned with investigating potential detection methods to replace the Dräger tubes. The sensors being evaluated in phase two are carbon dioxide (CO_2), hydrogen cyanide (HCN), hydrogen chloride (HCl), and broad range hydrocarbons (BRH). In this phase, the Dräger Multiwarn II and the Enmet Omni 4000 demonstrate good performance for the detection of CO_2 and HCN. The poor performance and accuracy of the HCl and BRH sensors results are shown. Further investigations are needed to find suitable detection methods for HCl and BRH.

15. SUBJECT TERMS

Submarine air monitoring; Portable air monitors; Carbon dioxide; Hydrogen cyanide; Hydrogen chloride; Broad range hydrocarbons; Vapor detectors; Electrochemical sensors; Infra-red sensor

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PHASE II: LABORATORY INVESTIGATION OF PORTABLE INSTRUMENTS FOR SUBMARINE AIR MONITORING

1.0 BACKGROUND

The submarine atmosphere is a unique controlled and monitored environment in which sailors live and work for extended periods of time. Atmosphere monitoring is principally done with the Central Atmosphere Monitoring System (CAMS), which is used to monitor life gases, permanent gases and some trace constituents. However, seventeen different detectors, primarily colorimetric (Dräger) tubes, are currently used to supplement the atmosphere analysis measurements made aboard US Navy submarines. As summarized in Table 1, there are a variety of circumstances under which these measurements must be made. In many cases, weekly measurements are required to supplement information obtained from CAMS. However, critical measurements are also made after casualty situations, such as a fire, or in drills for casualty situations. For example, carbon dioxide (CO_2), carbon monoxide (CO), hydrogen cyanide (HCN), and hydrogen chloride (HCl) levels must be monitored in a compartment for two hours after a fire. In gas free engineering applications (checking spaces not normally occupied), spaces are checked for CO, CO_2, oxygen (O_2), and combustible gas levels prior to entry into a space. Table 1 summarizes the Dräger tubes that are required, the situations under which they must be used, and the measurement level at which they must be employed. This requires that a supply of tubes, costing $4000 per year per submarine, be placed on board. Detector tubes have a limited shelf life, usually 2 years, and may expire before use. Most importantly, Dräger tube measurements give relatively slow response, are tedious, and require careful handling to be truly accurate. Even if used completely as specified, there is a degree of subjectivity in reading the colorimetric reactions on the tube. Consequently, there is little faith placed in the results and drills with the tubes are seldom properly conducted. The submarine fleet has requested that these tubes be replaced with a more modern, less labor intensive measurement system. Given the state of development of gas sensing instrumentation, it is possible to replace many of the existing Dräger tubes with instruments that will incorporate more than one sensor at a time. While it is unlikely that all of the existing tubes can be replaced with sensor packages in a cost effective manner, a good portion of the tubes outlined in Table 1 can be replaced.

It should be noted, however, that the submarine atmosphere is a unique environment. Simple deployment of off-the-shelf technology as direct drop-in replacements, while possible in some cases, is not advisable. For example, deployment of electrochemical sensors for CO detection will not work unless cross sensitivity for hydrogen is eliminated or compensated. Hydrogen levels aboard the submarine can vary extensively but are allowed to rise as high as 10,000 ppm. Consequently, any CO sensor with cross reactivity for hydrogen will generate false alarms when operations such as battery charging are carried out. Other considerations of note are the absence of significant amounts of onboard storage for calibration standards and bulky equipment. Therefore sensors chosen for these applications must have long shelf lives and low drift so that constant recalibration, onboard or shore side, is not required. Finally, the replacement measuring devices must require a minimal amount of intervention by ship's force.

Manuscript approved January 29, 2004.

Table 1. Compounds Evaluated with Dräger Tubes in Submarines

Compound	90-Day limit (ppm)	24-hour limit (ppm)	1-hour emer-gency limit (ppm)	Measure-ment range (ppm)	Weekly	Damage Control	Escape and Rescue	Gas-free Engin-eering
Acetone	200	1000	6000	20-9000	X			
Ammonia	50	100	100	0-150	X		X	
Benzene	1	2	50	0.1-75	X			
Carbon Dioxide	0.5%	4%	4%	0.05%-6%	CAMS X	X	X	X
Carbon Monoxide	20	50	400	2-600	CAMS X	X	X	X
Chlorine	0.1	0.5	3.0	0.05-4.5	X		X	
Combustible Gas				10% LEL to 25% LEL				X
Hydrocarbons	60 mg/m^3			6-600 mg/m3	X	X		
Hydrochloric Acid	0.5	20	20	0.05-30	X	X	X	
Hydrogen Cyanide	1.0	4.0	4.5	0.5 - 50		X	X	
Hydrogen Sulfide	1.0	3.0		2-500	X	X	X	
Monoethanolamine Ammonia	0.5	3	50	0.05-75	X			
Nitrogen Dioxide	0.5	1	1	0.05-1.5	X		X	
Oxygen	130-160 torr	130-160 torr	130-220 torr	100-250 torr	CAMS X	X	X	X
Ozone	0.02	0.1	1.0	0.005-1.5	X			
Sulfur Dioxide	1	5	10	0.1-15	X		X	
Toluene	20	100	200	2-300	X			
1,1,1-trichloroethane	2.5	10	25	0.25-37.5	X			

The technical objective of this effort was to procure, and test in the laboratory and aboard ship cost-effective replacements for the Dräger colorimetric tubes used for gas measurements aboard Navy submarines. In this effort, NSWC-CD/Philadelphia and Naval Research Laboratory (NRL), in consultation with NAVSEA, established a priority list of Dräger tubes to be replaced with appropriate handheld, portable sensors. The goal is to select replacement sensors that will cover as many applications (e.g. weekly atmosphere analysis, casualty etc) as is practicable. Once priorities were established, candidate sensor packages were selected. The sensor packages were selected to a) address measurement priorities and appropriate measurement ranges with sufficient accuracy, precision, and long-term reliability; b) maximize the number of sensors in a given instrument to minimize the number of instruments that need to be procured; c)

minimize the size and cost of the selected instruments; d) minimize the amount of calibration and replacement parts required. The test program was divided into three sections. Phase I used instruments that measured O_2, CO, hydrogen sulfide (H_2S), and combustibles (%LEL). Phase II evaluated responses to CO_2, hydrogen cyanide (HCN), and hydrogen chloride (HCl), and broad range hydrocarbons (BRH). Phase III will evaluate sensors for nitrogen dioxide (NO_2), ammonia (NH_3), sulfur dioxide (SO_2), chlorine (Cl_2), and ozone (O_3). This report describes Phase II laboratory test results. NRL was responsible for testing the sensors in the laboratory, assessing sensitivity, precision, accuracy and long-term drift of the instruments, as well as testing for cross sensitivity based on knowledge of the submarine atmosphere.

2.0 INTRODUCTION

Identification, selection and procurement of equipment for testing was based on the needs described in Table 1 and the priorities identified above. Candidate instruments were selected for testing using the following initial selection criteria:

a. **Measurement range**: From 10% of the 90-day limit to 50% above the 1 hour limit
b. **Environmental:** Temperature range: 20-50 °C, relative humidity 35-95%
c. **Interferences**: Cross sensitivities between sensors will be investigated. Hydrogen inference, particularly on the CO sensor is critical in these studies.
d. **Accuracy**: Short-term accuracy; ± 10% relative over the specified measurement range, within 10 minutes of calibration. Long-term accuracy; ± 25% relative over the specified measurement range for up to 1 year after calibration
e. **Reproducibility**: ± 10% for measurements made within 10 minutes, over entire measurement range.
f. **Size**: Less than 0.5 cubic foot volume.
g. **General features**: Rugged, reliable, user friendly and field compatible, with capability to integrate several sensors into the same platform
h. **Cost:** Integrated procurement and maintenance calibration costs over the instrument lifetime not to exceed the cost of equivalent number of Dräger tubes over the same period

Two different portable instruments are being utilized for Phase II testing. These are the Dräger Multiwarn II (Dräger) and the Enmet Omni 4000 (Omni). These two instruments are the same instruments used in Phase I testing with a different array of sensors. There are only two units used instead of the six that were used for Phase I testing because the appropriate sensors are only available for these two units. The sensors being used for Phase II testing are carbon dioxide (CO_2), hydrogen cyanide (HCN), hydrogen chloride (HCl), and broad range hydrocarbons (BRH). The Dräger has only the CO_2 and the HCN sensors available to test and the Omni is equipped with all four sensors although only three of these four sensors can be tested at once due to the instrument configuration. The Omni does have four sensor channels, but channel 1 is reserved for the detection of explosive gases, and the toxic sensors do not fit in the explosive sensor slot. Channel 2 must be occupied by the infrared CO_2 smart block and that leaves channel 3 and 4 for the BRH, HCN, and HCl sensors. These three test vapors cannot be applied

simultaneously because the HCN sensor responds to HCl and the BRH sensor responds to HCN. Therefore these three sensors are switched in and out accordingly. Appendix A gives the manufacturers' specifications for each sensor evaluated.

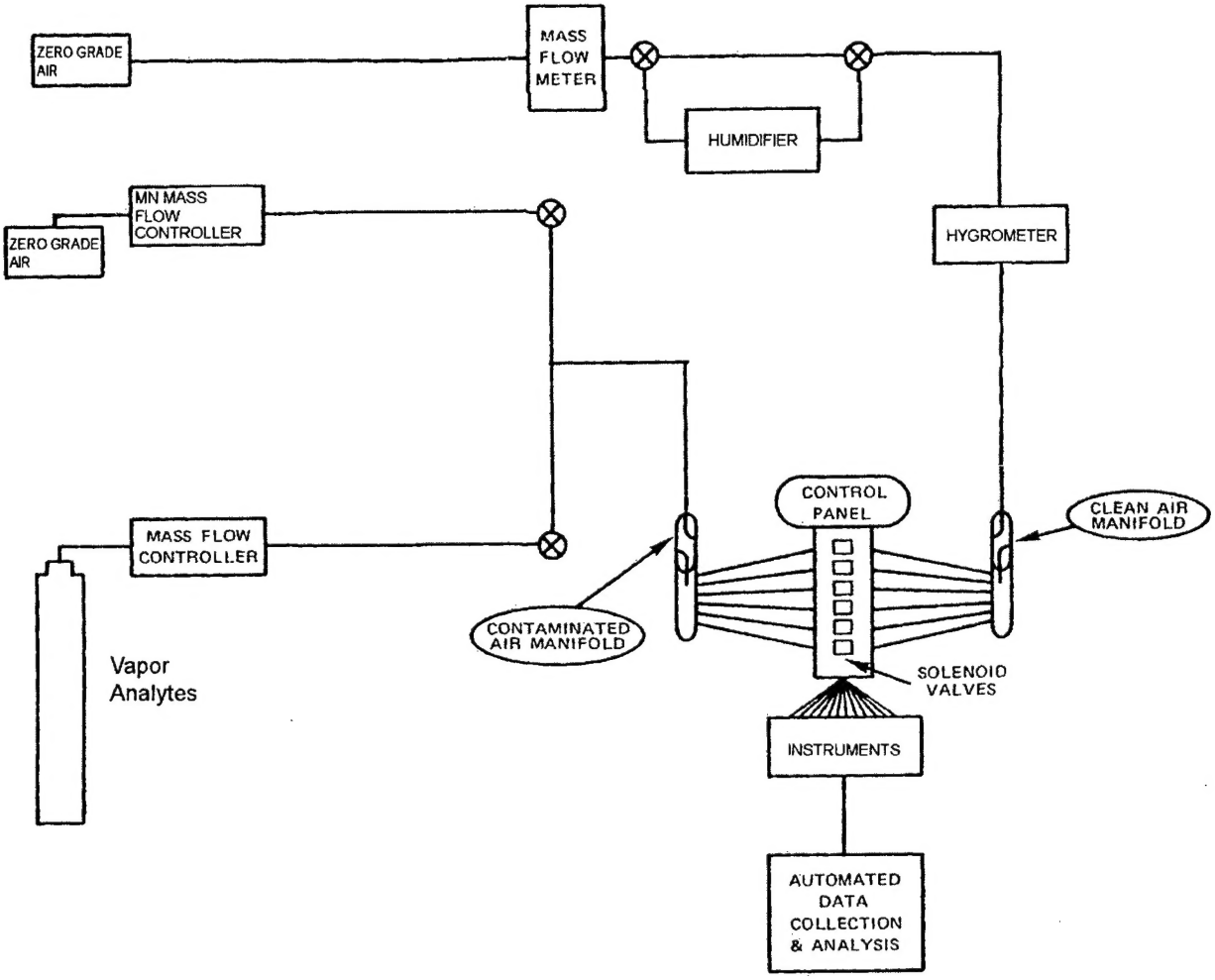
Phase II laboratory testing, similar to Phase I, was designed to evaluate the precision and accuracy of the sensors. Laboratory testing included short-term testing, interference testing, and weekly long-term testing. Short-term testing included exposures to single components repeated over several days, and interference testing was composed of hydrogen exposures as well as varying relative humidity exposures. Long-term testing consisted of weekly exposures of all compounds lasting 118 days. There was a gap in the middle of long-term testing for HCN and BRH sensors because the calibrated gas standards were depleted prematurely. Testing resumed when new HCN and BRH gas cylinders became available. The CO_2 and HCl sensors were tested over the entire time period and that data is used in the evaluation of the long-term performance.

3.0 EXPERIMENTAL

A vapor generation system was configured using mass flow controllers and a mixing chamber to generate a known concentration in a given relative humidity (RH) air. Zero-grade air was generated by passing house-compressed air through a series of demisters to remove any oil vapors, a reciprocating dual-tower molecular sieve scrubber, a hydrocarbon trap, and finally through a Purafil canister. The air was humidified to the desired level by passing it through distilled, deionized water. A Miller-Nelson Flow Control System is used to control the temperature and humidity of the purified air. For most tests, the air was kept at approximately 25°C with 50% relative humidity. Calibrated gas cylinders are used to generate the test vapors at a given concentration. Matheson and/or Tylan Mass Flow Controllers are used to control the flow of the test gases. These gases are mixed with clean air to create a specific concentration of analyte. Each test instrument sampled the same air off the sample manifold. Figure 1 shows a diagram of the test manifold used.

The test protocol is described below. The instruments were exposed to clean, humidified air for 5-10 minutes, then the test vapor for 5-10 minutes, and finally to the clean air for 5-10 minutes. They were not exposed to another test vapor until they had fully cleared down. Instruments were re-zeroed as needed in clean air. Short-term testing was completed upon receipt of the sensors. The instruments were exposed to test vapors across the entire measurement range. The effects of relative humidity were determined by exposing the instruments to the entire range of test vapor concentrations in dry, low, medium and high levels of RH. The instruments were evaluated for cross sensitivities by exposing them to single component samples. The hydrogen cross sensitivity was thoroughly evaluated. Long-term tests were conducted weekly over several months.

Figure 1. Test manifold designed for the instrument evaluation.



4.0 RESULTS

4.1 Short -Term Testing

Short-term testing consists of multiple exposures of single components. These tests are performed to specifically assess the instruments' factory calibrations and to determine any cross sensitivities among sensors. The data collected in this time period serves as a quantitative measure of the performance of the senseors' factory calibration. The primary hydrocarbon mixture used to test the Omni BRH sensor was a 50/50 Benzene and Octane mix. Other hydrocarbon gases used for experimental testing on the BRH sensor were Methane (CH_4), Benzene (C_6H_6), and Formaldehyde (HCHO) which were all applied individually.

4.1.1 Single Component Exposures

Single component exposures were performed to properly verify the consistency and accuracy of the sensors' factory calibrations and to determine any cross sensitivity among the four test gases. The units were exposed to each test gas three separate times at five different concentrations each. Figures 2-7 below contain the six plots of all six individual sensors; two of which are for the Dräger and four are for the Omni. These plots represent sensor responses versus applied concentration. The equations for each plot shown are representative of the response of each sensor. A slope of 1, an intercept of 0, and a R^2=1 are representative of an ideal response for short term performance.

Figure 2. Omni CO2 - Response vs. Applied Concentration

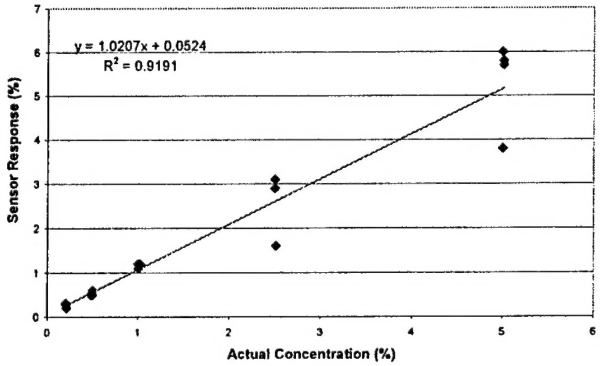


Figure 3. Drager CO2 - Response vs. Applied Concentration

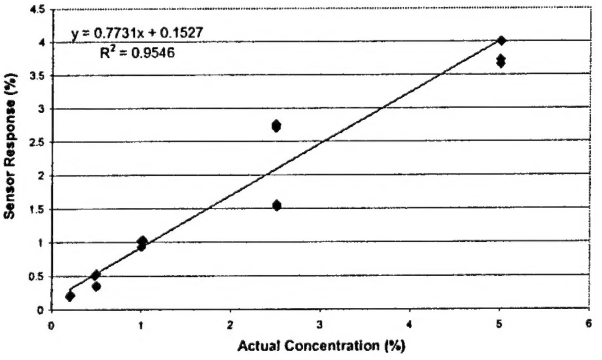


Figure 4. Omni HCN - Response vs. Applied Concentration

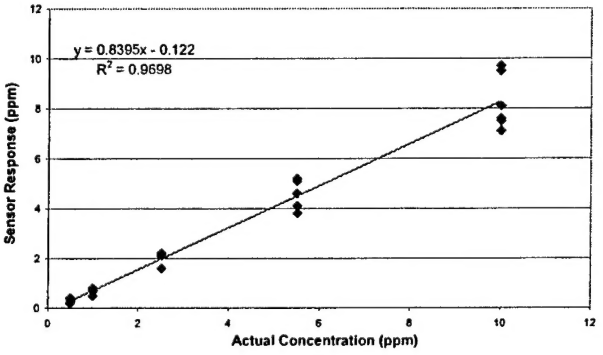


Figure 5. Drager HCN - Response vs. Applied Concentration

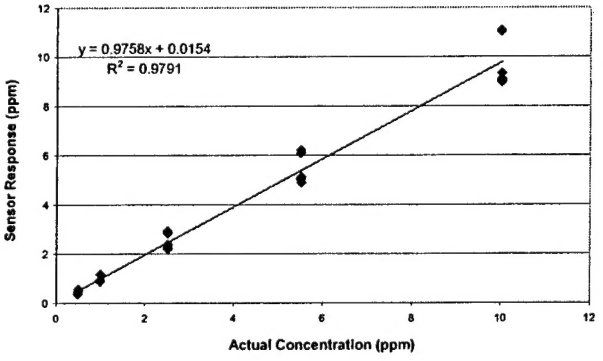


Figure 6. Omni HCl - Response vs. Applied Concentration

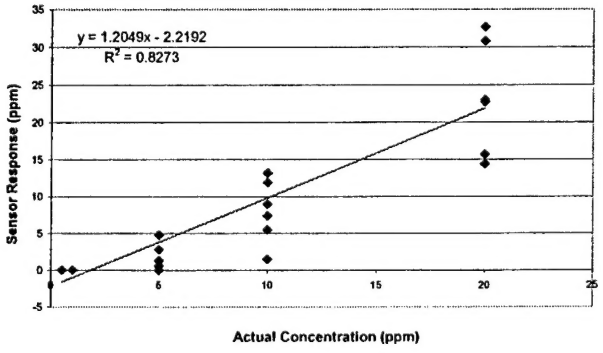
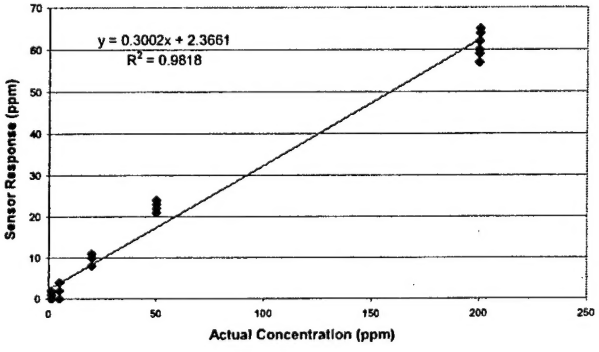


Figure 7. Omni BRH - Response vs. Applied Concentration



Having reviewed the factory calibration, short-term performance of all six sensors on the basis of slope, intercept, and R^2 the sensors ranked from better to worse in this category: Dräger HCN, Omni CO_2, Omni HCN, Dräger CO_2, Omni BRH, Omni HCl. The Dräger HCN sensor has good linearity and accuracy. This is the only sensor that performed effectively overall. The responses of the two CO_2 sensors and the Omni HCN sensor demonstrate less precision and accuracy. The Omni BRH and HCl sensors performed the worst. The Omni BRH sensor provides a linear response, but the accuracy is poor and the Omni HCl sensor demonstrated much scatter.

A summary of short-term, factory calibration performance data is provided here in Table 2. Note that the sensors are listed from top to bottom in order of best to worst performance.

Table 2. Factory Calibration, Short-term Performance

	Slope	Intercept	R^2
Dräger HCN	0.9758	0.0154	0.9791
Omni CO_2	1.0207	0.0524	0.9191
Omni HCN	0.8395	0.122	0.9698
Dräger CO_2	0.7731	0.1527	0.9546
Omni BRH	0.2961	3.0418	0.9838
Omni HCl	1.2049	2.2192	0.8273

Perfect sensor response: slope=1, intercept=0, R^2=1

Because the Omni BRH sensor is nonspecific to any one particular compound other single component exposures were performed on this sensor to obtain a wide range of data for proper verification of its effectiveness. Figures 8, 9, and 10 represent the response of the BRH sensor to hydrocarbons such as Methane (CH_4), Benzene (C_6H_6), and Formaldehyde (HCHO). There is much scatter for each of these vapors and accuracy is poor. The Omni BRH sensor performance is poor for all the hydrocarbons tested.

Figure 8. Omni - BRH Sensor Response to CH4

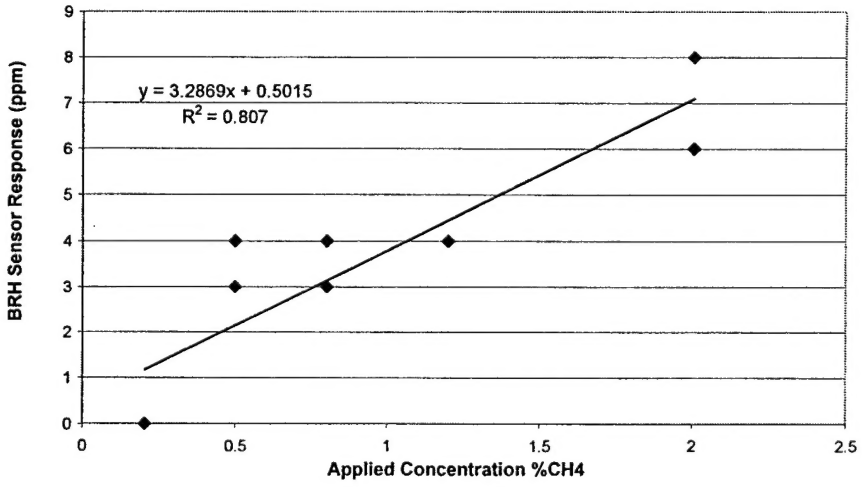


Figure 9. Omni - BRH Sensor Response to C6H6

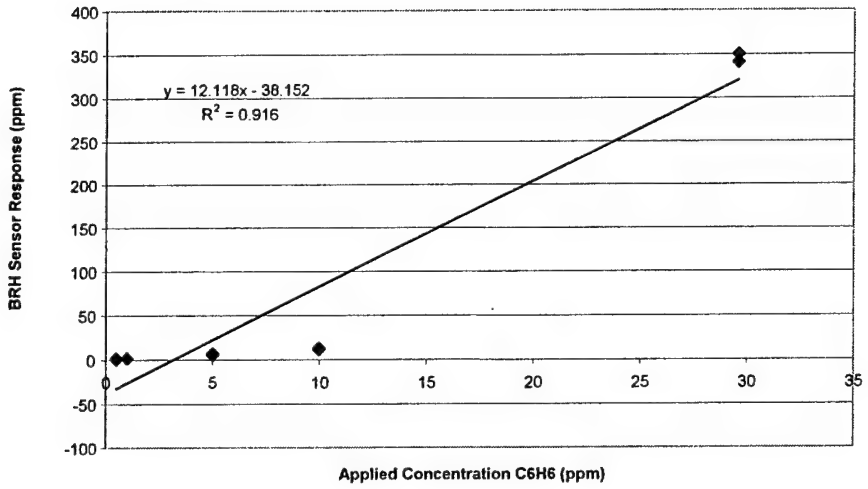


Figure 10. Omni - BRH Sensor Response to HCHO

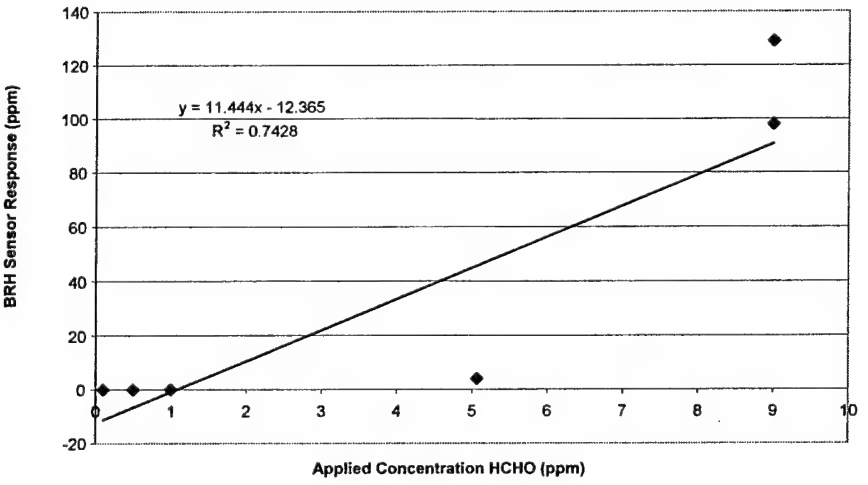
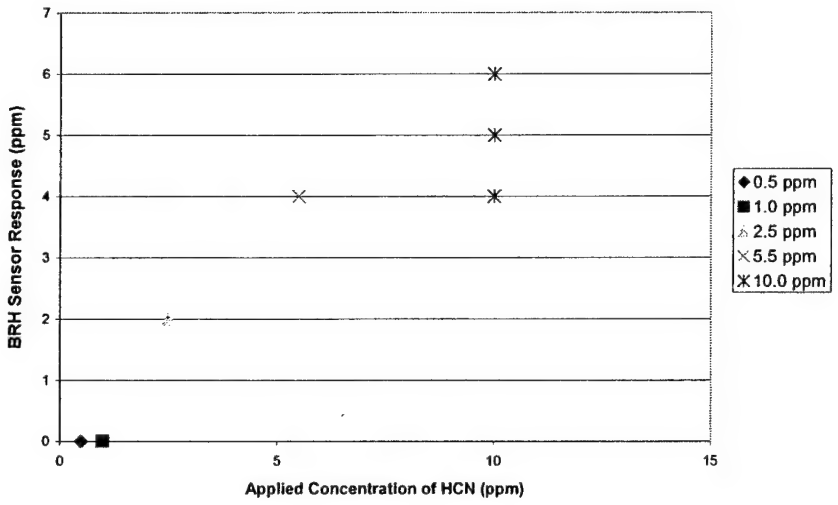


Figure 11. Omni BRH Sensor Response to HCN

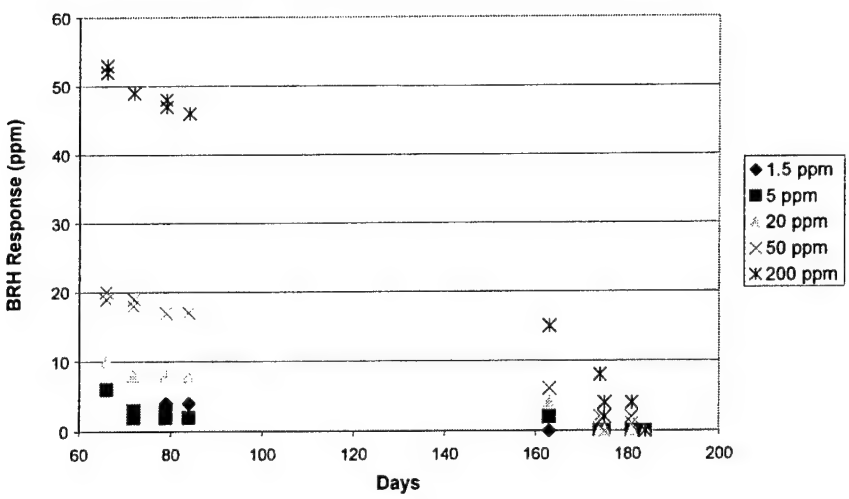


4.1.2 Cross Sensitivity

The cross sensitivity of the individual test vapors on each sensor was determined. The Omni BRH sensor has a considerable sensitivity to HCN gas. Figure 11 shows the BRH response for five different concentrations of HCN. In view of the Omni BRH sensors response to HCN gas, the test gas mixtures were modified for the last half of the long-term testing. Initially CO_2, HCN, and BRH were applied to the instruments simultaneously and HCl was tested separately because there are not enough sensor openings in the Omni to test all four sensors at once. Later, the experiment was modified to test the CO_2 and HCN sensors together and the HCl and BRH sensors together. Overall, the BRH sensor seems to respond better to HCN then it does to hydrocarbons and is verified through this modification. The Omni HCN sensor demonstrates a negative response to HCl gas and eventually goes into a fault mode when higher concentrations of HCl are applied. Therefore, the Omni HCl and HCN sensors were never tested at the same time to ensure the proper operation of the Omni HCN sensor. The Dräger HCN sensor showed no response to HCl gas.

Furthermore, Figure 12 is representative of the Omni's BRH sensor response where days 66 to 85 represent the response of the BRH sensors when HCN, BRH, and CO_2 gases were applied simultaneously, and days 162 to 181 represent the response of the BRH sensor when just BRH and HCl were applied together. The data indicates that the BRH sensor in the presence of HCN provides responses that are low, but consistent with the applied concentration. The responses in the presence of HCl dropped. Given that the BRH sensor has not shown any sensitivity to HCl, the BRH sensor seems to be losing sensitivity as time passes.

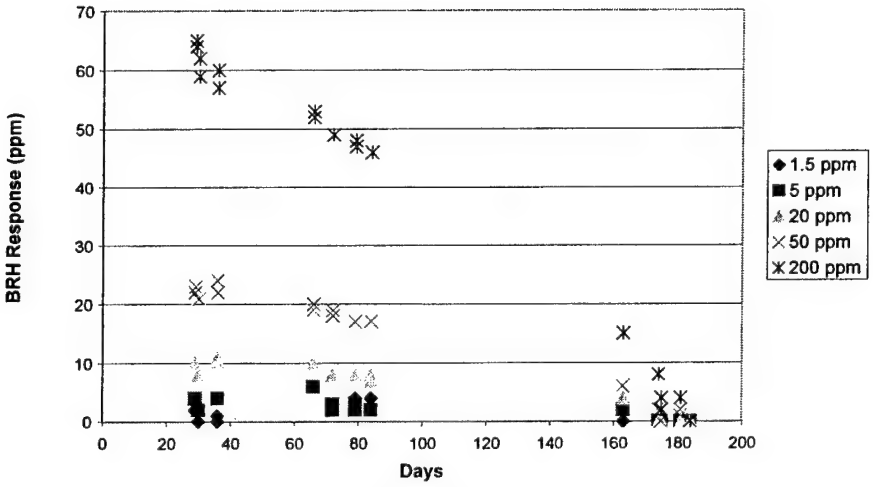
Figure 12. Omni BRH Performance



Day 66 - Day 85: HCN, BRH, & CO_2 applied simultaneously
Day 162 - Day 181: only BRH & HCl applied simultaneously

Figure 13 represents the BRH sensor response for the three single component tests performed before long-term testing started along with the long-term data. Days 29, 30, and 36 are the three single component test dates. The original factory calibration of the BRH sensor was never adequate enough to give an accurate response. One last single component test on day 184 confirmed that the Omni BRH sensors calibration did in fact fail. The BRH sensor showed no response to any applied concentration of the Benzene/Octane mixture.

Figure 13. Omni BRH Performance



Day 29 – Day 36: Single Component BRH tests
Day 66 – Day 85: HCN, BRH, & CO_2 applied simultaneously
Day 162 – Day 181: only BRH & HCl applied simultaneously

4.2 Interference Testing

4.2.1 Hydrogen Cross Sensitivity

Hydrogen (H_2) levels aboard submarines can vary extensively and therefore the hydrogen cross sensitivity was evaluated. H_2 only provides a response on the Omni BRH sensor and the Dräger HCN sensor. Figures 14 and 15 below show the responses of the Omni BRH sensor and the Dräger HCN sensor to a H_2 concentration ranging from 0.003% to 0.100% H_2 respectively. The Dräger HCN sensor response to H_2 is small. At 0.10% H_2 (1000 ppm) the Dräger HCN sensor gives a response of 0.68 ppm HCN. This is higher than desirable, but below the Navy 90-day exposure limit. The BRH sensor response gives a 235 ppm for the same concentration of H_2. This response is too great for the sensor to be useful in the submarine environment.

Figure 14. Omni - H2 Interference on BRH sensor

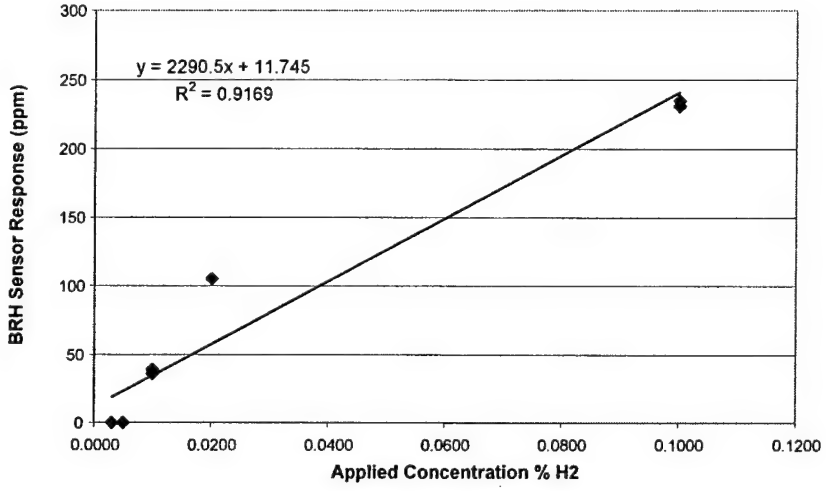
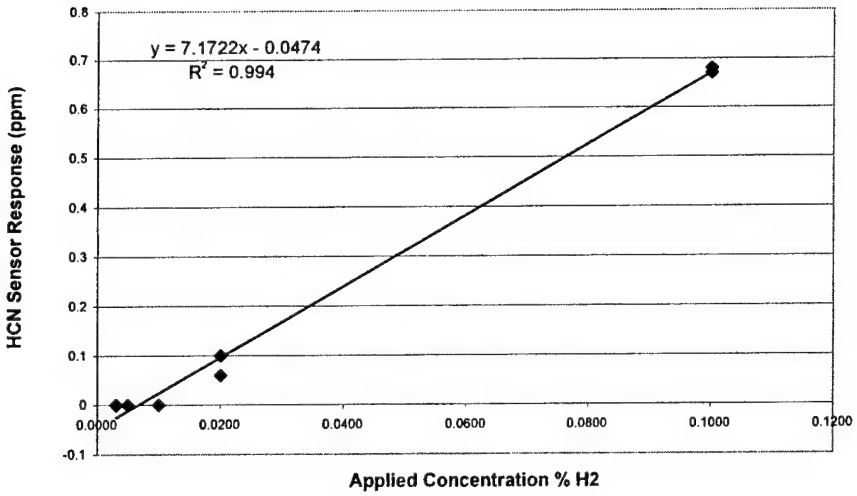


Figure 15. Drager - H2 Interference on HCN sensor



4.2.2 Humidity Testing

Relative Humidity testing was performed between day 37 and day 63. All six sensors were tested at 0%, 30%, and 85% relative humidity. Three different concentrations of each test gas were applied to the sensors individually during each experiment. As with Phase I sensors, these tests confirmed that all six sensors show no significant sensitivity to variations in relative humidity.

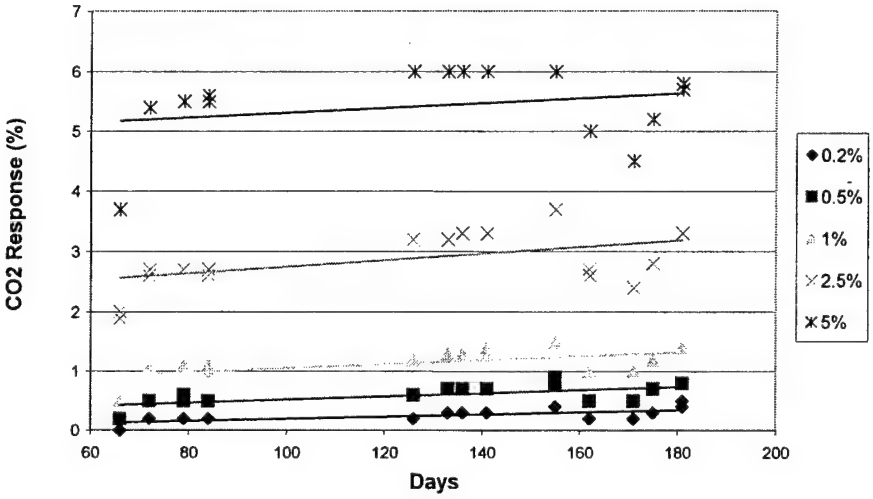
4.3 Long -Term Testing

Phase II long-term testing consisted of weekly exposures of all four test vapors to the sensors. This testing began on day 66 and was concluded on day 198. In the first four weeks of testing, days 66 – 85, both HCN sensors, the Omni BRH sensor, and both CO_2 sensors were tested simultaneously and the Omni HCl sensor was tested separately. Unfortunately, both the HCN and the Benzene/Octane gas cylinders were emptied during these exposures and testing on the HCN and BRH sensors was halted until new tanks arrived on day 161. In the meantime, both the CO_2 sensors and the Omni HCl sensor were tested weekly. After the new tanks arrived, testing began again utilizing a modified procedure. Following the analysis of the HCN interference on the BRH sensor, the new procedure had the HCN and CO_2 sensors tested together and the HCl and BRH sensors tested together. This modification proved that the Omni BRH sensor did not respond as expected to the hydrocarbon mixture and eventually experienced calibration failure and gradually lost all sensitivity to hydrocarbons.

4.3.1 Long -Term Carbon Dioxide Sensor Performance

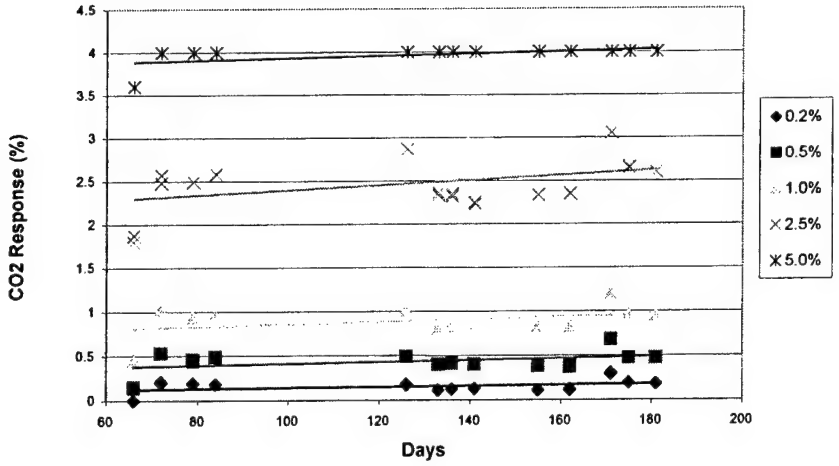
The long-term performance of both the Omni and Dräger CO_2 sensor was comparable and satisfactory. As stated earlier, day 66 – day 85 was the original test plan in which HCN, BRH, and CO_2 were all tested simultaneously. From day 126 – day 155 the CO_2 and HCl sensors were tested together and from day 162 – day 181 the CO_2 and the HCN sensors were tested together. No other test vapor affects the performance of the CO_2 sensors, as verified during single component testing. Figures 16 and 17 show the long-term response for both sensors. Typically, the Omni CO_2 sensors' response is, on average, 0.4% higher than the delivered concentration and the Dräger CO_2 sensors' response is, on average, 0.4% lower than the delivered concentration.

Figure 16. Omni CO2 Sensor Performance



The Omni CO_2 sensor performance is reasonably constant for the duration of tests. The abrupt drop on day 162 which continued to day 171 is due to the fact that this sensor was removed from its analyzer unit between days 155-162 and also between days 162-171. During this time, other sensors were placed into the analyzer unit for a different experiment. The CO_2 sensor was put back into the Omni analyzer on day 162 for the weekly exposure and on day 171. The non-consistent response is due to lack of warm-up time in the analyzer before the weekly testing started. The response on day 181 appears to be similar to the earlier performance.

Figure 17. Drager CO2 Performance



The Dräger CO_2 sensor is more precise and accurate than the Omni CO_2 sensor for the interval of the long-term tests. This CO_2 sensor is an infrared sensor which cannot be removed from its analyzer unit. The abnormally high response on day 171 may be due to a series of usual tests conducted on the instrument. Between days 162 and 171 the Dräger analyzer was used to evaluate a different set of sensors. Nitrogen Dioxide (NO_2), Ammonia (NH_3), and Sulfur Dioxide (SO_2) sensors were installed. These sensors were all tested with the appropriate test vapors. The cross sensitivity of these test vapors will be evaluated in Phase III. For both sensors the quality of the factory calibration remained consistent for the duration of the long-term tests. Table 3 below provides a summary of the average long-term Carbon Dioxide sensors response data.

Table 3. Carbon Dioxide, % by volume, Long-term Sensor Performance

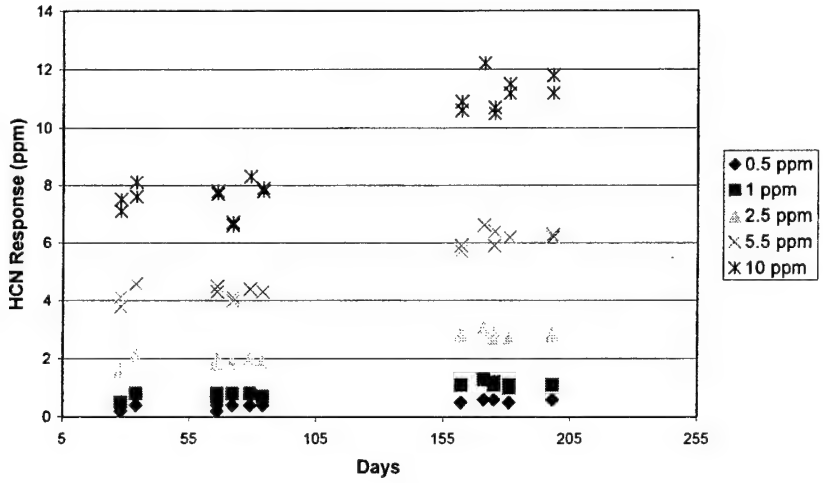
Instrument	Range	Precision	Accuracy
Dräger CO_2	0.2% - 0.5%	+/- 0.1%	0.1% low
	1.0%	+/- 0.2%	0.2% low
	2.5%	+/- 0.3%	0.3% low
	5.0%	+/- 0.1%	1.0% low
Omni CO_2	0.2%	+/- 0.1%	0.1% high
	0.5%	+/- 0.2%	0.2% high
	1.0%	+/- 0.3%	0.3% high
	2.5%	+/- 0.5%	0.6% high
	5.0%	+/- 0.7%	0.8% high

4.3.2 Long -Term Hydrogen Cyanide Sensor Performance

As stated earlier, the HCN sensors for both instruments were tested in two different ways. Day 66 – day 85 are the responses of the sensors when HCN, BRH, and CO_2 are applied simultaneously and day 162 – day 181 are the responses when only HCN and CO_2 are applied. In addition, a new calibrated gas cylinder was used beginning on day 162. The difference in

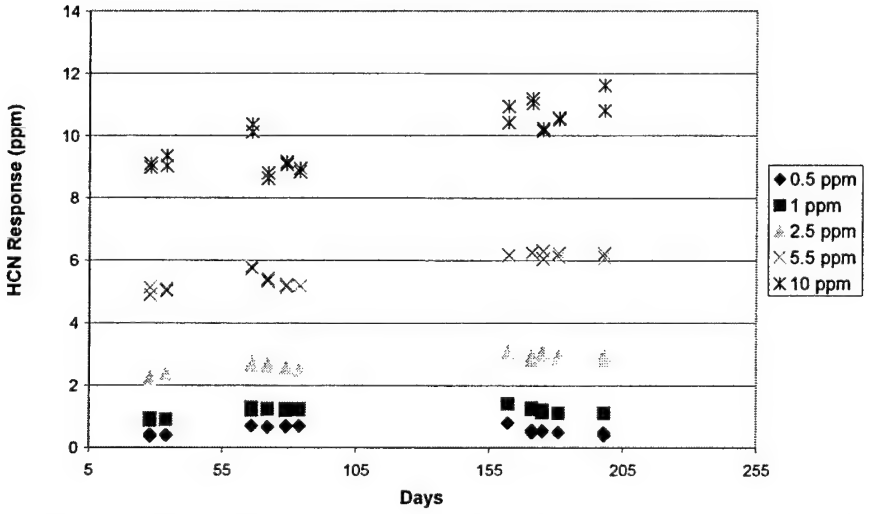
responses is obvious for the Omni HCN sensor when the new gas cylinder was used. The difference in responses for the Dräger HCN sensor is not as apparent but the sensor does respond higher than in earlier tests. Also, the data for the original single component tests is represented in the figures below on day 28 and day 34. Another single component test was performed on day 198 with the new gas cylinder for analysis verification. Both of these sensors have held their factory calibrations throughout the period of long-term testing.

Figure 18. Omni HCN Performance



Day 28 – Day 34: HCN Single Component test (old gas cylinder)
Day 66 – Day 85: HCN, BRH, & CO_2 applied simultaneously (old gas cylinder)
Day 162 – Day 181: only HCN & CO_2 applied simultaneously (new gas cylinder)
Day 198: HCN Single Component test (new gas cylinder)

Figure 19. Drager HCN Performance



A summary of both HCN sensors responses during long-term testing with each gas cylinder is provided in Tables 4 and 5. The Omni HCN sensor gives the same response to HCN in the presence of the benzene/octane mixture. The Dräger and Omni HCN sensors show an increase in response with the new gas cylinder. The gas cylinder calibration is likely off by 10 – 20%. The accuracy of the two instruments is similar; however the Dräger is more precise than the Omni.

Table 4. Hydrogen Cyanide, ppmv, Long-Term Sensor Performance (old gas cylinder)			
Instrument	**Range**	**Precision**	**Accuracy**
Dräger HCN	0.50 – 1.00 ppm	+/- 0.15 ppm	0.20 ppm high
	2.50 ppm	+/- 0.30 ppm	0.20 ppm high
	5.50 ppm	+/- 0.30 ppm	0.40 ppm low
	10.00 ppm	+/- 0.90 ppm	1.00 ppm low
Omni HCN	0.50 ppm	+/- 0.10 ppm	0.20 ppm low
	1.00 ppm	+/- 0.20 ppm	0.30 ppm low
	2.50 ppm	+/- 0.20 ppm	0.70 ppm low
	5.50 ppm	+/- 0.90 ppm	1.00 ppm low
	10.00 ppm	+/- 2.00 ppm	2.50 ppm low

Table 5. Hydrogen Cyanide, ppmv, Long-Term Sensor Performance (new gas cylinder)			
Instrument	**Range**	**Precision**	**Accuracy**
Dräger HCN	0.50 ppm	+/- 0.10 ppm	0.20 ppm high
	1.00 ppm	+/- 0.10 ppm	0.30 ppm high
	2.50 ppm	+/- 0.30 ppm	0.50 ppm high
	5.50 ppm	+/- 0.50 ppm	0.70 ppm high
	10.00 ppm	+/- 1.00 ppm	0.90 ppm high
Omni HCN	0.50 ppm	+/- 0.10 ppm	0.10 ppm high
	1.00 ppm	+/- 0.30 ppm	0.20 ppm high
	2.50 ppm	+/- 0.60 ppm	0.40 ppm high
	5.50 ppm	+/- 1.00 ppm	0.80 ppm high
	10.00 ppm	+/- 2.00 ppm	1.50 ppm high

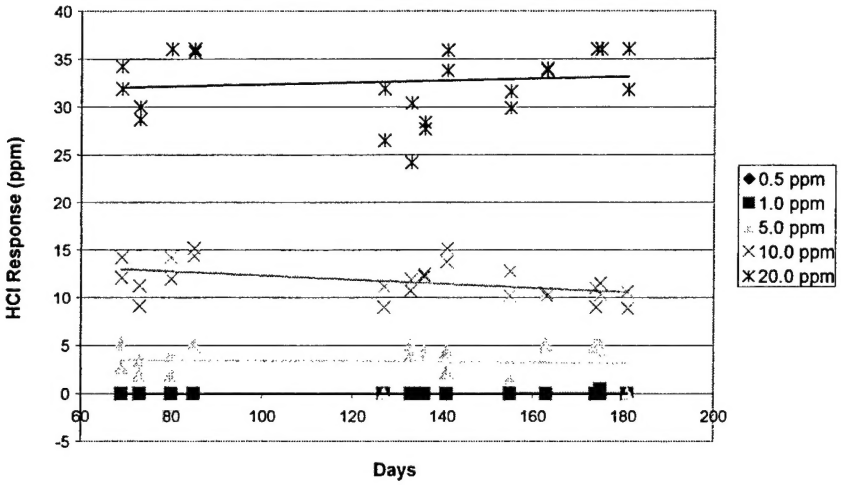
On the whole, both sensors have very good precision and accuracy particularly when responding to lower concentrations and would be suitable to use in a submarine atmosphere.

4.3.3 Long -Term Hydrogen Chloride Sensor Performance

The Omni analyzer was the only unit equipped with a Hydrogen Chloride Sensor. This sensor performed very poorly during the short-term testing, but it was able to maintain that level of performance during the long-term testing. During long-term testing, it has been noted that not only is this sensor inconsistent but it also takes a very long time to respond to the HCl gas. It sometimes took as long as thirty minutes for the HCl sensor to respond and just as long for it to clear out. Another factor observed is that the sensor performs better towards the end of testing after it has gone through multiple exposures. By the end of a weekly test, which can take up to eight hours, the sensor does perform more quickly, but not necessarily more accurately. Figure 20 shows the performance of the HCl over the long-term interval. Again, as with the CO_2

testing, the first set of data points are the responses when just HCl is supplied to the sensor, the second set of data points are the responses when HCl and CO_2 are applied to the sensor simultaneously, and the third set of points are the responses when HCl and BRH are applied together. Neither CO_2 nor BRH has an affect on the HCl sensor.

Figure 20. Omni HCl Performance



Day 69 – Day 85: Only HCl applied
Day 127 – Day 155: HCL & CO2 applied together
Day 163 – Day 181: BRH & HCl applied simultaneously

The HCl sensor does not respond at all to the lowest concentrations (0.5 & 1.0 ppm) and responds consistently low at the middle concentration (5.0 ppm). However, for the highest two concentrations (10.0 & 20.0 ppm) the sensor responds typically high. Table 6 provides a summary of the HCl long-term sensor performance.

Table 6. Hydrogen Chloride, ppmv, Long-Term Sensor Performance

Instrument	Range	Precision	Accuracy
Omni HCl	0.5 ppm	+/- 0 ppm	0.5 ppm low
	1.0 ppm	+/- 0.1 ppm	1.0 ppm low
	5.0 – 10.0 ppm	+/- 2 ppm	2.5 ppm low (5 ppm)/ high(10 ppm)
	20.0 ppm	+/- 3.5 ppm	13 ppm high

4.3.4 Long -Term Broad Range Hydrocarbon Sensor Performance

Like the Hydrogen Chloride sensor, the Broad Range Hydrocarbon sensor was only available for the Omni analyzer. The performance of this sensor was, by far, the worst out of the six sensors being tested. In addition, this is the only sensor to fail at the end of long-term testing. Returning to the Cross Sensitivity section of this paper, (see Figures 12 and 13), the long-term

performance of this BRH sensor is represented in Figure 13. The responses for the last four weeks of testing (days 163 – 181) proved that the sensor was losing its sensitivity and then an extra single-component test was performed on day 184 that verified that the sensor completely failed. It had no response to any concentration of the hydrocarbon mix. A summary of the Omni BRH sensor long-term performance up to day 181 is provided in Table 7.

Table 7. Broad Range Hydrocarbon, ppmv, Long-Term Sensor Performance			
Instrument	**Range**	**Precision**	**Accuracy**
Omni BRH	1.5 ppm	+/- 2.0 ppm	2.0 ppm low
	5.0 ppm	+/- 2.0 ppm	4.0 ppm low
	20.0 ppm	+/- 4.0 ppm	16.0 ppm low
	50.0 ppm	+/- 8.0 ppm	40.0 ppm low
	200.0 ppm	+/- 20.0 ppm	180.0 ppm low

Additionally, a summary of the performance of the Omni BRH sensor for just the three single component tests is provided in Table 8. A comparison of the two tables shows similar accuracy. The precision of the sensor is much better during single-component tests.

Table 8. Broad Range Hydrocarbon, ppmv, Single-Component Sensor Performance			
Instrument	**Range**	**Precision**	**Accuracy**
Omni BRH	1.5 ppm	+/- 1.0 ppm	1.0 ppm low
	5.0 ppm	+/- 1.0 ppm	2.0 ppm low
	20.0 ppm	+/- 1.0 ppm	12.0 ppm low
	50.0 ppm	+/- 1.0 ppm	30.0 ppm low
	200.0 ppm	+/- 3.0 ppm	150.0 ppm low

5.0 CONCLUSION

After analysis of all six Phase II sensors, (Enmet Omni 4000 – CO_2, HCN, HCl, BRH sensors & Dräger Multiwarn II – CO_2, HCN sensors) the Dräger Multiwarn II CO_2 and HCN sensors prove to give the best overall performance compared to the Omni CO_2 and HCN sensors. However, the difference between their performances is very small. Either instrument will accurately measure CO_2. Given the data, the Omni HCN sensor would typically perform well with the CO_2 sensor and most likely an Oxygen and LEL sensor. However, the Omni's Operation and Maintenance Manual states that the HCN sensor does have a slight interference to Phase I gases (CO and H_2S) and Phase III gases (NO_2 and Cl_2). It also states that this sensor has an unpredictable interference with a Phase III gas (SO_2) and up to +/- 4 ppm interference with another Phase III gas (NH_3). The most reliable configuration of the Omni analyzer when using the CO_2 and HCN sensors would be with an Oxygen and LEL sensor since there are no reported interferences. The Omni's manual also states that the CO_2 and BRH sensors decrease the operational life of the unit considerably. The battery life of the Omni analyzer with a CO_2, BRH,

and other toxic sensors is reported to be a maximum of eight hours without the pump and six hours with the pump turned on. Taking all this into consideration, the Dräger analyzer is the best instrument to use when measuring HCN.

The Omni HCl sensor would be difficult to use in the submarine environment. The HCl sensor possessed no interferences with any other Phase II gas, but frequent calibration and a sufficient amount of time for the unit to warm-up would have to be performed in order to achieve adequate performance. In addition, this sensor never responded to HCl at 0.5 ppm or 1.0 ppm. The measurement range for HCl evaluated with Dräger tubes in submarines is 0.05 ppm – 30.0 ppm. As of now, the sensitivity of the Omni HCl sensor is not adequate enough to measure low concentrations. Perhaps future sensors will be. The Omni BRH sensor is not suitable for submarine applications.

Unlike Phase I laboratory testing, Phase II sensors did not experience calibration failure after only two - three months. Testing was performed for approximately six months and the only sensor to fail was the Omni BRH sensor. The Carbon Dioxide and Hydrogen Cyanide sensors demonstrate good performance and would be expected to do so for at least six months. Suitable sensors for Hydrogen Chloride and Broad Range Hydrocarbons have not been identified. Further investigations are necessary.

Appendix A

Vendor	Name of Portable Analyzer	Number of Sensors	Sensor Technology	Interchangeable Electrochemical Sensors	CO2 Measurement Range	HCN Measurement Range	HCl Measurement Range	Broad Range Hydrocarbons Measurement Range	Power Source	Battery Life	Durability/ Warranty	website
Dräger	Multiwarn II	5	3 electrochemical plus combustible sensor (catalytic combustion) plus IR sensor for CO_2	Yes	0 to 25% vol.	0 to 10 ppm	No available sensor for this instrument	No available sensor for this instrument	NiCad	8 hours	3-5 years	http://www.draeger.com/us
EnMet Corporation	OMNI-4000	4	3 Smart Blocks (electrochemical) plus Combustible Sensor (catalytic combustion)	Yes	0 to 5%	0 to 10 ppm	0 to 30 ppm	0 to 500 ppm	NiCad battery pack; Lithium battery for data storage	12 -14 hours for NiCad battery; 3-5 years for lithium battery	1 year	http://www.enmet.com